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Overview of High-Temperature Electrolysis for Hydrogen Production

Safety and Technology of Nuclear Hydrogen Production, Control, and Management (ST-NH2)

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Overview of High-Temperature Electrolysis for Hydrogen Production

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INTRODUCTION

Over the last five years there has been a growing interest in the use of hydrogen as an energy carrier, particularly to augment transportation fuels and thus reduce our dependence on imported petroleum. Hydrogen is now produced primarily via steam reforming of methane. However, in the long term, methane reforming is not a viable process for the large-scale hydrogen production since such fossil fuel conversion processes consume non-renewable resources and emit greenhouse gases.

Nuclear energy can be used to produce hydrogen without consuming fossil fuels and without emitting greenhouse gases through the splitting of water into hydrogen and oxygen. The Nuclear Hydrogen Initiative of the DOE Office of Nuclear Energy is developing three general categories of high temperature processes for hydrogen production: thermochemical, electrolytic and hybrid thermo-electrolytic. This paper gives a brief overview of the work being done in the development of high temperature electrolysis of steam.

High Temperature Electrolysis (HTE) is built on the technology of solid oxide fuel cells (SOFCs), which were invented over a century ago, but which have been most vigorously developed during the last twenty years. SOFCs consume hydrogen and oxygen and produce steam and electricity. Solid Oxide Electrolytic Cells (SOECs) consume electricity and steam and produce hydrogen and oxygen. The purpose of the HTE research is to solve those problems unique to the electrolytic mode of operation, while building further on continuing fuel cell development.

A schematic of the operation of a hydrogen production plant using the heat and electricity of a high temperature nuclear reactor is shown in Figure 1. About 80 % of the thermal energy of the reactor, at ~900° C, is sent to the Brayton of the efficient (~50%) generation of electricity. The remaining 20% is used to heat the reagent water to steam at about 850 °C. The a mixture of 90 vol % steam and 10 vol % hydrogen is fed to the electrolytic cells, where the oxygen migrates through the electrolyte at $O^{=}$ ions because of the imposed voltage. The voltage necessary is about 0.3 V lower than in conventional electrolyzers because of the high operating temperature. In addition the kinetics of the electrolytic reactions are much faster than in room temperature electrolysers, thus avoiding polarization losses. The mixture existing the cells, about 25 vol % steam and 75 vol %hydrogen, enters a separation device contain a porous inorganic membrane through which the hydrogen diffuses three times more rapidly because of its molecular weight of 2, compared to 18 for the steam. Most of the steam and some of the hydrogen is mixed with additional steam, reheated and returns to the electrolytic cells. The remaining steam can be removed from the hydrogen product stream through condensation. Like the hydrogen stream, the oxygen stream exiting the cells has a temperature of about 830° C. An integrated HTE plant would contain heat exchangers to transfer the heat of the hydrogen to in the coming water or steam. The oxygen might be cooled or it might be used in high temperature combustion processes.

In addition, the integrated operation of the electrolytic plant offers the utility the potential to vary the output from hydrogen to electricity within a few minutes. We have found in experiments with stacks of electrolytic cells that the out can be changed from full hydrogen production of zero by simply controlling the voltage applied to the cells. By operating at either the thermal neutral voltage or the open cell voltage, the output can be varied without imposed thermal transients on the cells. When the cell voltage is reduced, the steam continues to flow through the stacks, maintaining the 830° C operating temperature, but no current flows and no hydrogen is produced.

Thus the utility could respond to variation in the grid demand by producing less hydrogen or by accepting power from the grid and producing hydrogen beyond the capability of the reactor alone.

ORGANIZATION

Experiments have been conducted for the last four years at the Idaho National Laboratory and at Ceramatec, Inc. on the operation of button cells and of progressively larger stacks of planar cells. In addition, the INL has been performing analyses of the cell-scale fluid dynamics and plant-scale flowsheets in order to determine optimum

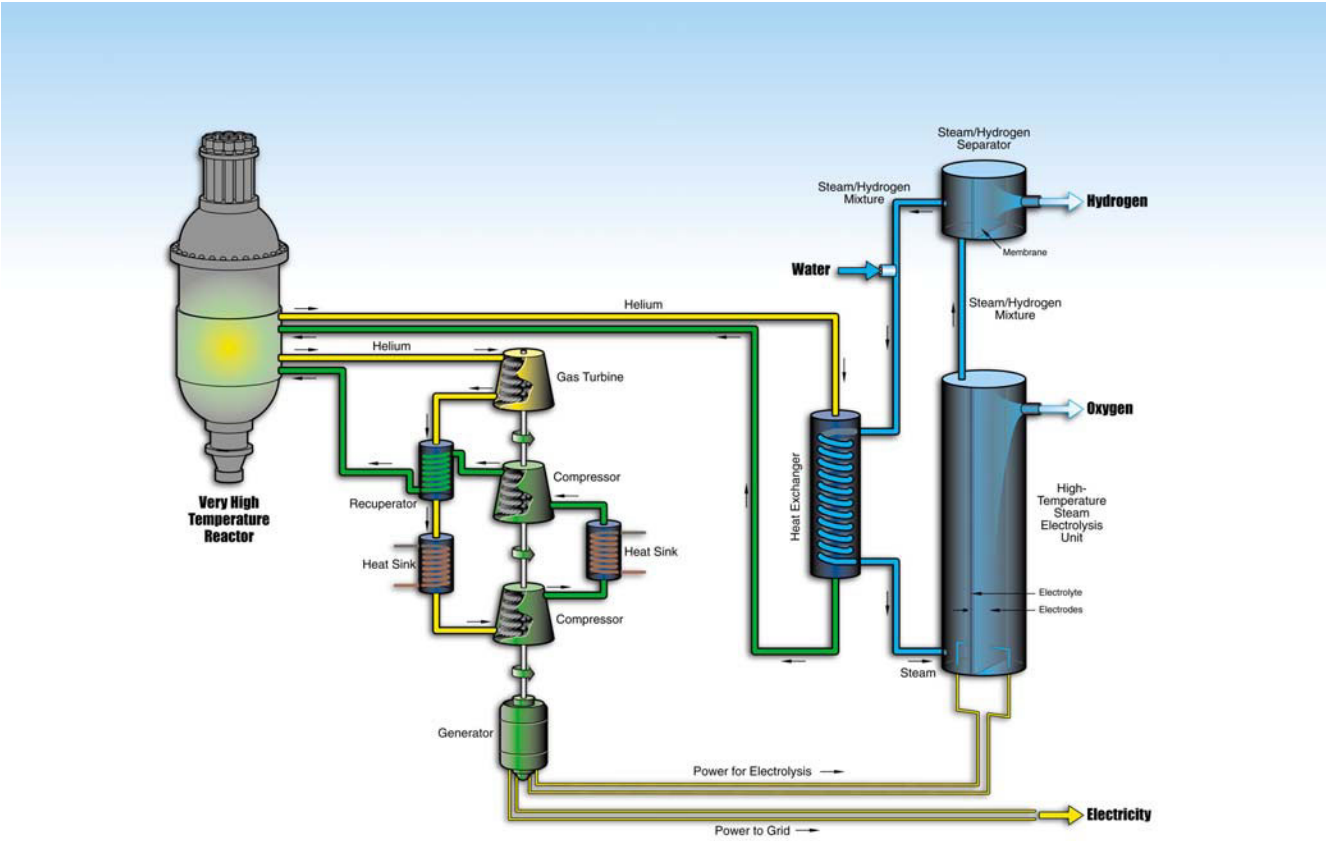

Figure 1. Nuclear powered high temperature electrolysis.

operating conditions and plant configurations. Argonne National Laboratory has been performing experiments for the development of new electrode materials, as well as modeling of the fluid dynamics and flowsheets for comparison with the work being done at the INL. ANL has also been performing diagnostic measures on components form long-duration tests at the INL and Ceramatec to determine the causes for the slow degradation in cell performance. Oak Ridge National Laboratory has been developing high temperature porous membranes for the separation of hydrogen from the residual steam, thus avoiding the need to condense and reheat the steam. The University of Nevada at Las Vegas has been collaborating with ANL on the development of electrode and electrolyte materials and will soon begin to investigate the causes of cell degradation. HTE research also includes NERI projects at the Virginia Polytechnic Institute on the development of toughened SOEC composite seals and at the Georgia Institute of Technology on the microstructural design of SOEC materials.

Papers in this session will describe in greater detail the experimental and analytic work being done at these institutions.

EXPERIMENTAL RESULTS

The most recent large-scale test of HTE was performed from June 28 through Sept 22, 2006 at the Ceramatec plant in Salt Lake City. The test apparatus, shown in Figure 2, consists of two stacks of 60 cells each in a configuration that will be used in the Integrated Laboratory Scale (ILS) experiment during FY-07. The ILS will contain three modules of four stacks each. The "Half-Module," which is about 30 cm wide and high and 15 cm deep, initially produced 1.2 normal $m^3$of H_2/hour and 0.65 Nm^3/hr at the end of the 2040-hour continuous test. The steam/hydrogen mixture enters the two stacks from either side and flows through the cells to the center manifold, exiting at the top as about 75% hydrogen, 25% steam. Heated air is supplied to a plenum on the opposite side of the two stacks and an mixture of air and oxygen exits through the opening visible in the front. More details on this experiment will be presented by Hartvigsen.

DIAGNOSTIC RESULTS

Carter, et al , examined the components tested in July 2005, Jan-Feb 2006 and June-Sept 2006, tracking the migration of elements in the cells, the local four-point

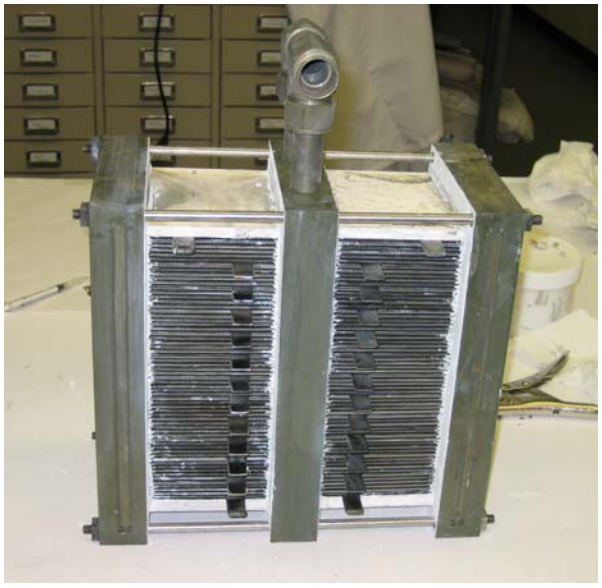

Figure 2. Half-Module tested summer 2006. Steam (+ ~10v/o H_2) enters through the manifolds on either end. Hydrogen (+~25 v/o residual steam) exits through the fitting at the center. Oxygen exits stack through the cell edges in the front. Tabs are for current supply and equalization.

resistance of the electrodes and instances of electrode-electrolytic delamination or cracking. An example of those measurements is shown in Figure 3. Further details will be presented by Carter in this session.

Figures 3 and 4 show some of the work being done by Carter and co-workers at Argonne to investigate the causes for the long-term degradation in stack output that has been seen in the last three tests. Chief among the suspected causes for the slow increase in cell area specific resistance (ASR) are delaminations between the electrolytes and the electrodes, transport of metals for the interconnect or silica from the sealants and small cracking or other imperfections in the electrolyte. Determining the causes of this degradation a prime focus in the HTE work for the coming years.

FUTURE PLANS

The design for the Integrated Laboratory Scale (ILS) experiment is complete and the fabrication/assembly of components is beginning. The ILS will contain three modules of four 60-cell stacks each, for a total of 720 cells. The experiments should produce ~5 Nm3/hour. The ILS will also contain the various vaporizers, superheaters, steam-hydrogen separators and heat recuperators needed to demonstrate, at a reduced scale, all of the components of a commercial HTE plant.

The ILS electrolyzer will consist of three modules, each comprised of four 60-cell stacks. Figure 1 is an artist rendering of the 4-stack module. All three modules will be located within one hot zone as shown in Figure 5. The electrolysis modules require a support system supplying electrical power for electrolysis, a feedstock gas mixture of hydrogen and steam, a sweep gas, and appropriate exhaust handling. In particular, this system must include means for controlled steam generation, mixing hydrogen with the steam, feedstock and product dewpoint measurements, heating the feedstock and sweep gas to the appropriate electrolysis temperature, cooling the electrolysis product stream, condensing any residual steam out of the product stream, and venting both the hydrogen product and sweep gas stream.

The ILS is designed such that each electrolysis

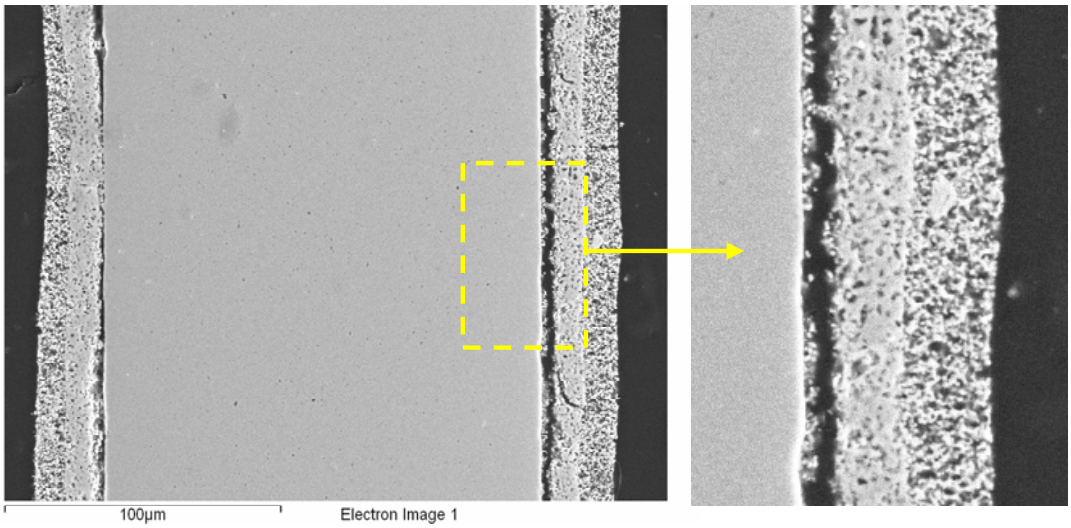

Figure 3. SEM image of CER11, showing delamination at the electrolyte-electrode interface, and over-sintering of the inner layer active electrode. Both the delamination and over-sintering can lead to short-term and long-term performance loss at the electrode.

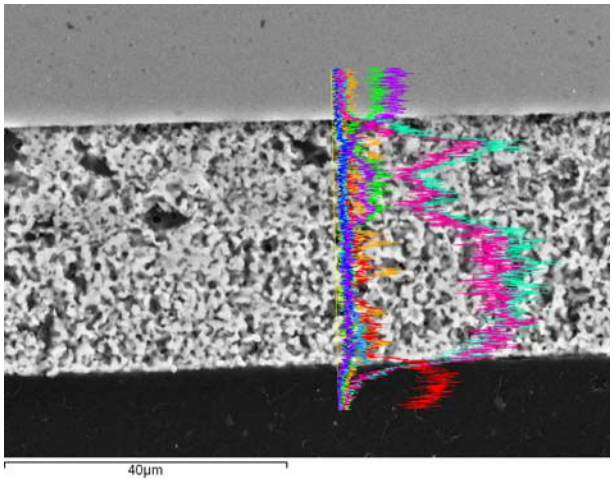

Figure 4. The air electrode 2 cm away from the sealed edges of the 25-cell stack, tested 1000 hours, Jan-Feb, 2006. The overlaid lines are EDS line scans of the various elements in the electrode.

module has its own independent support and instrumentation system. The feedstock and product gas streams for each electrolysis module are monitored and controlled separately and thus the inlet and outlet gas composition and flow rate is known for each module. If a module failed during operation, that particular module could be shut down without affecting the performance or testing of the other modules. And since each module is operated and monitored separately, they can have different operating conditions (feedstock and electrical parameters) at the same time. In this way, a test matrix covering a range of operating conditions could be covered more quickly.

The initial configuration without heat recuperation or hydrogen recycle is shown in Figure 5. The facility is designed such that later insertion of heat recuperation equipment and hydrogen recycle can be accommodated. Figure 6 presents a rendering of the initial ILS configuration, and with important components labeled. Further details on the design of the ILS will be presented in the paper by Housley in this session.

The initial ILS electrolysis module containing four stacks of 60 cells each has been completed and delivered. The design of the full module closely follows the design of the half-module tested June-Sept. 2006 by Ceramatec. The four stacks of the initial module are shown in close-up in Figure 7.

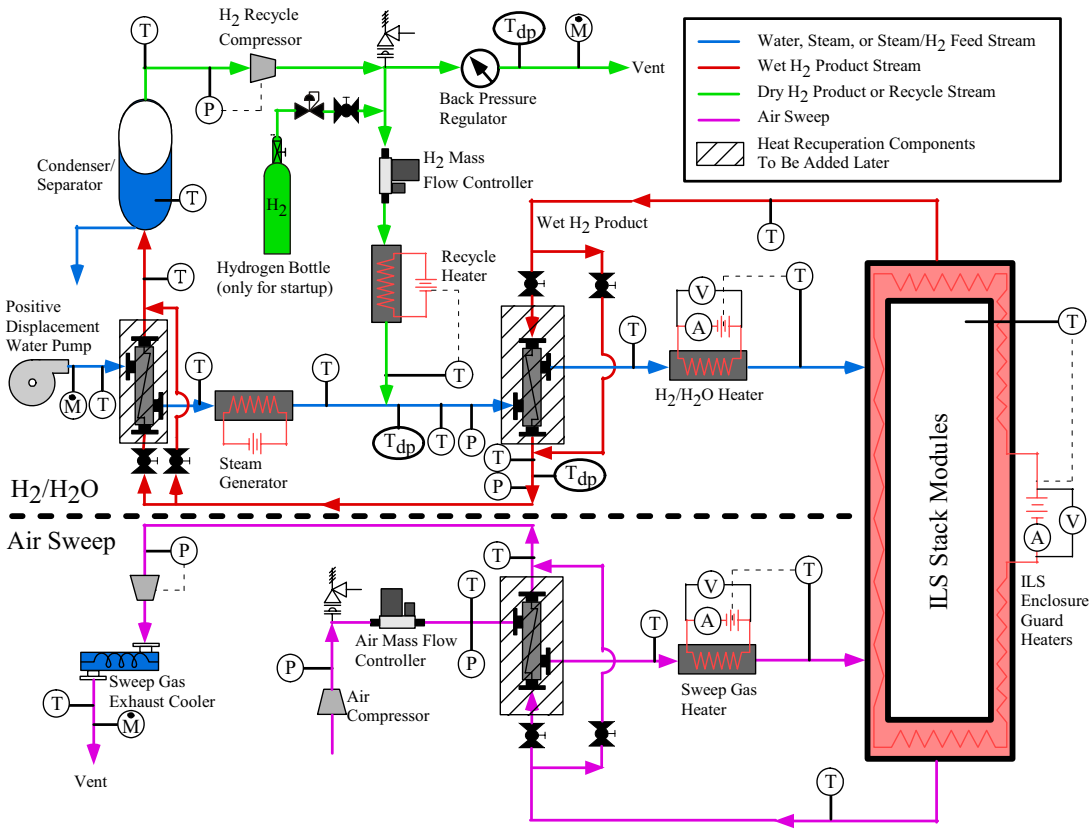

Figure 5. High Temperature Electrolysis Integrated Laboratory Scale experiment

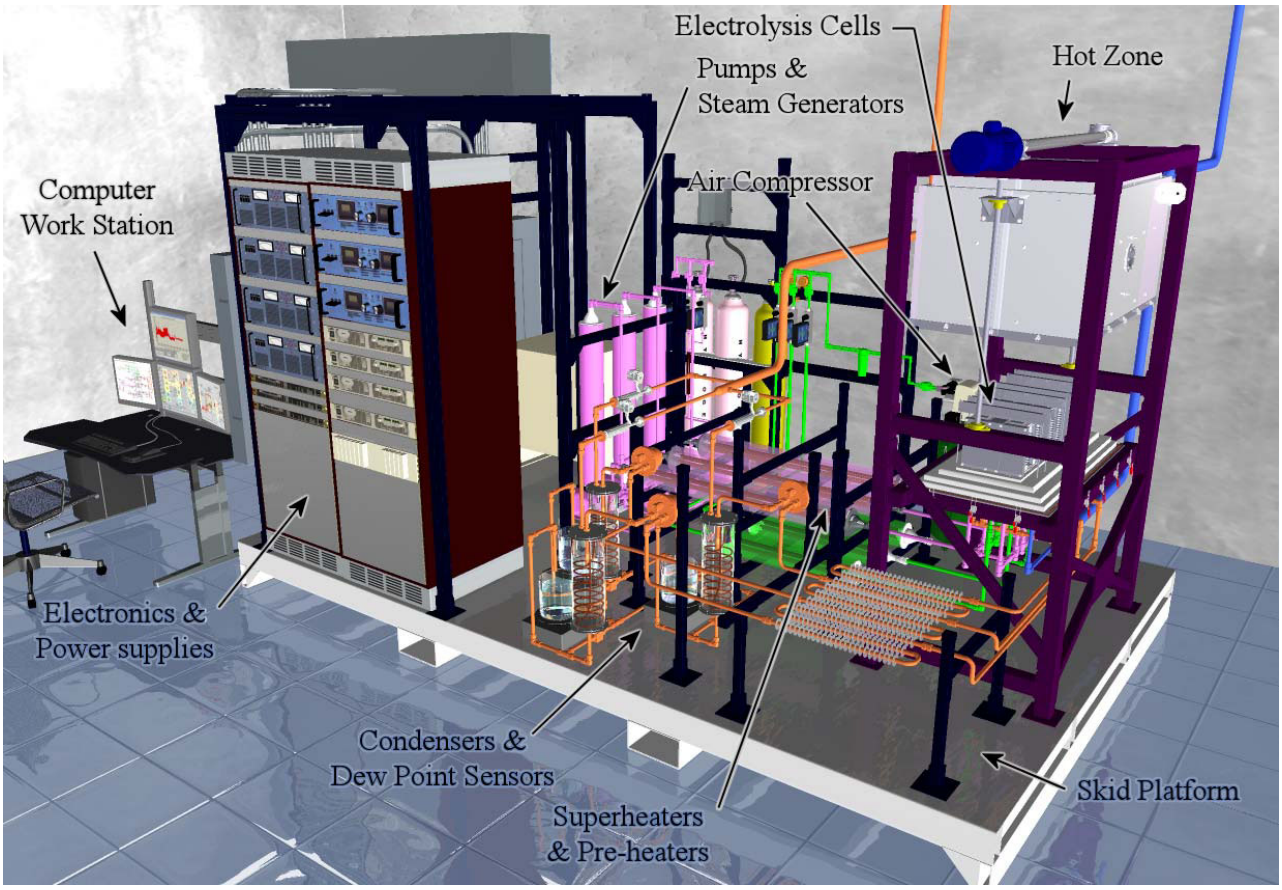

Figure 6. ILS experiment perspective view. Electrolytic cells are at the right end of the experimental skid.

Co-Electrolysis of CO_2 and H_2O

Under a separately funded project at the INL, we have been investigating the use of solid oxide cells for the co-electrolysis of CO_2 and H_2O according to the reaction

$$2\ H_2O + CO_2 \rightarrow 2\ H_2 + CO + 1.5\ O_2$$

The resulting carbon monoxide and hydrogen, known as "synthesis gas" has been used for nearly a century for the production of hydrocarbon fuels through the Fischer Tropsch synthesis

$$n\mathrm{CO} + (2n+1)\mathrm{H_2} \rightarrow \mathrm{C_nH_{2n+2}} + n\mathrm{H_2O}$$

The alkane C_nH_{2n+2} can be a wide range of hydrocarbons from diesel and jet-fuel to wax. Our reason for exploring the production of synthesis gas for hydrocarbons is that, in the near-term, these fuels are essential for our transportation needs. Furthermore, the infrastructure of pipelines, gas stations and vehicles already exists and will not be soon or easily replaced. Finally, as summarized in the statements below, liquid hydrocarbons have some distinct advantages when compared to gaseous hydrogen.

O'Brien, Stoots and Hawkes will discuss modeling and experiments performed at the INL on the production

Figure 7. The four stacks of the initial module for the ILS experiment. The faces shown will be joined to a plenum which will provide hot air to carry the oxygen out of the cells. The tabs shown are used to equalize the voltages among the stacks. The main current leads are on the opposite of the stacks

of synthesis gas through co-electrolyis in three papers in this session.

REFERENCES

Carter, J. David, Ann Call, Magali Ferrandon, Jeremy Kropf, Victor Maroni, Jennifer Mawdsley, Deborah Myers, and Bilge Yıldız, "High-Temperature Steam Electrolysis Cell and Stack Diagnostic Results," Argonne National Laboratory report, November 29, 2006

Table 1: Characteristics of liquid fuels and hydrogen for transportation

Gasoline, diesel and jet fuels are:

- ***Liquid over range of ambient temperatures, -40° F to 130° F***
- ***Pumpable: a filling station gasoline pump, running at ~20 liters/min delivers energy at 11 MWth***
- ***Energy dense: gasoline or diesel ~34 MJth/liter at 0.1 MPa***
    - ***H_2 gas: 9.9 MJth/liter at 80 MPa, (11,000 psi)***

  [Hydrogen is more concentrated per unit mass – if one ignores the mass of the tank or hydride:
    - ***H_2: 120 MJ_{th}/kg, gasoline: 40 MJ_{th}/kg]***
- ***Storable: little loss, fire hazards understood***
- ***Transportable by pipeline:***

  the energy flow through a 36 in oil pipeline is 70 GW_{th}